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Article

Analysis of Seaweeds from South West England as a Biorefinery Feedstock

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Abstract: Seaweeds contain many varied and commercially valuable components, from individual pigments and metabolites through to whole biomass, and yet they remain an under cultivated and underutilised commodity. Currently, commercial exploitation of seaweeds is predominantly limited to whole biomass consumption or single product extracts for the food industry. The development of a seaweed biorefinery, based around multiple products and services, could provide an important opportunity to exploit new and currently underexplored markets. Here, we assessed the native and invasive seaweeds on the South West coast of the UK to determine their characteristics and potential for exploitation through a biorefinery pipeline, looking at multiple components including pigments, carbohydrates, lipids, proteins and other metabolites.

Keywords: marine; biorefinery; seaweed; lipid; carbohydrate; pigment; phytohormone; heavy metal

1. Introduction

Annually, over 25 million tons of macroalgal (seaweed) biomass is harvested globally, with the vast majority (95%) of this produced in Asia. The total market is currently worth \$5.6 bn, with food products for human consumption making up approximately \$5 bn of this [1] and the rest predominantly from animal feeds, fertilizer, pharmaceuticals and cosmetics. Recently, seaweed consumption by cattle has even been suggested as a useful way to decrease greenhouse gas emissions and combat climate change: when *Asparagopsis taxiformis* was used at 2% concentration in cattle feed, a significant reduction in methane production was observed [2]. With limited space for agricultural expansion in the terrestrial environment, the exploitation of seaweeds is gaining increasing attention in regions not traditionally associated with its mass cultivation and consumption. Whilst direct human consumption arguably remains the most easily accessible market in these “new” regions, a lack of cultural and social awareness and/or acceptance of the benefits will most likely hinder uptake. However,

beyond food/feeds consumption, there is potential for seaweeds to be used as valuable feedstocks for biorefineries producing multiple products aimed at alternative markets [3]. “Bio-refining” separates biomass into a range of fractionated products in an attempt to maximise the value and use of biomass. Combining the production of high-value specialty chemicals and nutraceuticals alongside lower value products, such as fuels, fertilisers, polymers and fillers, can create a sustainable production system where little to no waste flow is generated, therefore decreasing negative environmental impacts and improving economic viability [3,4].

Europe is attempting to increase its level of seaweed production; however, almost all this production is by wild harvest rather than active farming [5]. The UK, with its extensive coastline and temperate waters is ideal for high-value seaweed production; yet, it was estimated that in 2013, the seaweed production from wild harvest in the UK was merely 2000–3000 dry tonnes, providing a huge opportunity for growth [5]. Commercially, the seaweed harvesting sector in the UK is underdeveloped, with only 27 UK-based companies—mostly small- to medium-sized enterprises (SMEs)—harvesting and selling seaweed, and just 16 of those harvesting within UK coastal waters [5].

Within the UK, there has been a recent flurry of activity from the academic community on seaweed biomass conversion (albeit low value), seeking to develop simultaneously created multiple fuel and fertilizer products, rather than a sole wholefood product, suggesting the biorefinery approach could gain momentum [6]. Indeed, several trials for seaweed cultivation in the UK are currently underway across the South West where high levels of sunlight provide favourable growth conditions. Plans for a seaweed farm in the South West, which could produce biofuels, medicines and bioplastics was submitted to the Marine Management Organisation at the end of 2018 [7], and a European Maritime and Fisheries Fund supported project to trial off-shore cultivation techniques in the South West has recently been supported and will begin in the summer of 2019.

The potential interest in placing offshore wind farms in the South West may provide a potential site for co-cultivation with subsidised infrastructure costs; indeed, combining different commercial activities in a single area may help to mitigate the conflicts of interest that invariably arise when offshore waters are claimed for a variety of different, and often overlapping, uses [8]. However, even before the not insignificant regulatory hurdles can be overcome, the licence requirements must be ascertained and cultivation know-how established [5]; if this fledgling industry is to be successful, the identification of potential target markets outside of the limited domestic wholefood sector is of the utmost importance. A biorefinery-based approach is likely the most effective way to achieve this and has the added benefit of potentially being able to accept both natural harvest and cultivated seaweed biomasses and, crucially, has the potential to utilise biomasses of diverse origin (i.e., multiple species).

Whilst offshore cultivation provides plenty of scope for controlled, regulated and monitored activity around particular seaweed crops, increasing natural harvest levels of mixed communities by existing commercial entities may create an ecological imbalance and will need to be managed carefully. Yet, the harvesting of natural biomass to “sanitise” beaches to promote tourism is already an established and socially acceptable activity in the South West. For example, between 1 April 2018 and 28 June 2018, 734.8 tonnes of seaweed were collected (and sent for composting) from 18 beaches by Torbay council, giving an average monthly collection of approximately 248 tonnes during the peak of the tourist season (Personal Communication, Torbay council). Storm-generated beach material in the winter months also represents a significant biomass which could be used as feedstock for the generation of refined non-food-based products.

Assuming biomass generation and availability is not a limitation in the future, the question remains as to what exactly is/are the best input biomass(es) for a marine seaweed biorefinery in the South West. It is important to recognise that whilst seaweeds have a variety of different attributes, most of these are specific to individual species and so assumptions cannot be made about the potential of “seaweeds” as a crop without being tempered by the reality of what any given species can produce. There are a broad range of different seaweeds with different properties growing around the UK coast [9]

and these different species have a range of components that can make them valuable for the production of nutraceuticals, fuels, fertilisers and fine chemicals.

Here, we explored some of the components that can make individual seaweeds (commonly found in the South West) valuable as feedstocks in a biorefinery-based process, such as lipids and high-value omega oils, pigments with antioxidant and antibacterial properties, plant hormones and macronutrients, minerals, total carbohydrate and proteins. We avoided established food additives derived from seaweed sugars, such as agar and carrageenan, as they have been investigated previously and already offer established markets [1,10]. In addition, we also assessed heavy metal levels which could potentially hinder commercialisation opportunities.

2. Materials and Methods

2.1. Collection and Identification of Samples

Fresh seaweed samples (Table 1) were collected from Broadsands Beach (50°24′24.9″ N 3°33′16.2″ W), Oyster Cove (50°25′04.1″ N 3°33′20.9″ W) and Saltern Cove (50°24′57.9″ N 3°33′24.4″ W), Paignton, Devon, in May 2017. Seaweeds were visually identified using References [9,11] onsite, harvested and taken immediately to the laboratory for processing.

Table 1. Seaweed harvested on the South Devon coast from Broadsands Beach 50°24′24.9″ N 3°33′16.2″ W, Oyster Cove 50°25′04.1″ N 3°33′20.9″ W and Saltern Cove 50°24′57.9″ N 3°33′24.4″ W.

Species	Common Name	Taxon
<i>Ulva lactuca</i>	Sea lettuce	Chlorophyta
<i>Spongomorpha aeruginosa</i>	Spongy weed	Chlorophyta
<i>Polyides rotunda</i>	Discoid fork weed	Rhodophyta
<i>Lomentaria articulata</i>	Bunny ears	Rhodophyta
<i>Ahnfeltiopsis devoniensis</i>	Devonshire fan weed	Rhodophyta
<i>Palmaria palmata</i>	Dulse	Rhodophyta
<i>Rhodomela confervoides</i>	Straggly bush weed	Rhodophyta
<i>Dilsea carnosa</i>	Red rags	Rhodophyta
<i>Calliblepharis</i> spp.	Eye lash weed	Rhodophyta
<i>Gastroclonium ovatum</i>	Red grape weed	Rhodophyta
<i>Sargassum muticum</i>	Wireweed	Phaeophyta
<i>Himanthalia elongata</i>	Thong weed	Phaeophyta
<i>Fucus serratus</i>	Serrated wrack	Phaeophyta
<i>Laminaria digitata</i>	Oar weed/tangle	Phaeophyta
<i>Saccharina latissima</i>	Sugar kelp	Phaeophyta
<i>Punctaria latifolia</i>	n/a	Phaeophyta
<i>Colpomenia peregrina</i>	Oyster thief	Phaeophyta

2.2. Preparation of Seaweed

All samples were rinsed in filtered seawater to remove sand and other large particulates such as micro plastics, frozen at −80 °C and then freeze dried at −55 °C. Freeze-dried samples were ground to a fine powder that was stored in sealed containers at −80 °C to prevent sample degradation.

2.3. Pigment Extraction

To 50 mg dried seaweed, 2 mL of acetone was added along with 100 mg glass beads. Samples were then disrupted by rapid agitation in a bead beater for 3 min after which cell debris was settled by centrifugation. The supernatant (containing the extracted pigments) was analysed by high-performance liquid chromatography (HPLC) using an Accela system (Thermo Scientific, Waltham, MA, USA) fitted with a Waters Symmetry C8 Column (150 × 2.1 mm, 3.5 µm particle size, thermostatically maintained at 25 °C) according to the method of Zapata et al. [12]. Pigments were detected at 440 nm and 660 nm and identified by retention time and online diode array spectra. Monovinyl chlorophyll-a standard

was obtained from Sigma–Aldrich Ltd. and other pigment standards were purchased from the DHI Institute for Water and Environment, Denmark. Quality assurance protocols followed Reference [13].

2.4. CHN/Protein

A Thermoquest Flash EA 1112 Elemental Analyzer (Thermo Fisher Scientific, Inc.) with high-temperature dry combustion was used to measure the percentage of carbon and nitrogen in each sample. Per each seaweed, three technical replicate samples consisting of 2 mg of finely ground freeze-dried seaweed were analysed. The percentage of protein per seaweed was estimated using the percentage of nitrogen determined by CHN analysis multiplied by the N-Prot conversion factor 5.0, as described in Reference [14] rather than the traditional N-prot value of 6.25 [15], which is generally recognised as overestimating protein content in seaweeds.

2.5. Ash

Ten to 50 mg of freeze-dried powdered seaweed was ashed in a muffle furnace for 2 h at 650 °C, then cooled to room temperature for 30 min in a desiccating cabinet. The ash percentage was calculated by $(\text{final weight}/\text{initial weight}) \times 100$ for each of the samples.

2.6. Metal Analysis

Lithium tetraborate beads (10.2167 g) and 1.0000 g of seaweed were weighed and placed in a platinum crucible and heated in a Claisse electric Ox fusion furnace for a 1 h thermal cycle at 1050 °C. The fused borate beads were analysed by X-ray emission spectroscopy using the Panalytical Axios XRF Spectrophotometer.

2.7. Lipids

The fatty acid concentrations and profiles of the seaweed samples were determined post conversion to fatty acid methyl esters (FAMES) using GC–MS. To 7–11 mg freeze-dried finely ground seaweed, tridecanoic acid (C13:0) was added as an internal standard and cellular fatty acids were converted directly to FAMES by adding 1 mL of transesterification mix (1:1 *v/v* (methanolic–HCl); (chloroform: methanol 2:1)) followed by incubation at 70 °C for 1 h. After cooling, FAMES were recovered by addition of n-hexane (1 mL) followed by vortexing. The upper hexane layer was injected directly onto the GC–MS. The FAMES were identified and quantified using retention times and qualifier ion response. All parameters were derived from calibration curves generated from a FAME standard mix.

2.8. Phytohormones

Detection of four different bioactives (abscisic acid (ABA); trans-zeatine riboside (TZR); cis-zeatine riboside (CZR); and N6-(2-isopentyl) adenosine (2iP)) was achieved using Agrisera's plant hormone ELISA kits (Agrisera AB). The ELISAs were performed according to manufacturer instructions. Extractions were performed as follows: dry biomass (1 g) was resuspended in 100 mM acetate buffer (12 mL, pH 4.0) and vortexed for 2 min. Following sonication with a probe sonicator (6 times \times 30 s on-pulse and a 30 s off-pulse, amplitude 10 microns) in an ice bath, samples were centrifuged at 10,000 \times g, at 4 °C for 15 min. The pH was rechecked and returned to pH 4.0, if necessary, with acetic acid prior to solid phase extraction purification. The SPE Supra-Clean[®] C18-S Columns (50 mg/1 mL, PerkinElmer) were conditioned with 1 mL of methanol, equilibrated with 1 mL of 100 mM acetate buffer (pH 4.0) prior to the addition of 4 mL of extract. Following a wash with 1 mL of 5% methanol, the column was dried and 200 μ L of 100% methanol was added to the elute fractions.

3. Results and Discussion

Seaweeds potentially make excellent lignin-free feed stocks for biorefineries due to the large range of products that can be extracted and isolated from them such as oils, proteins, carbohydrates and

pigments. In addition, once high-value primary products have been refined, micronutrients can be recovered from the residual waste biomass.

In this study, 17 abundant and easily harvestable species of seaweed from the South West (see Table 1) were collected, identified and categorised by taxon—Chlorophyta (greens), Rhodophyta (reds) and Phaeophyta (browns). Seaweeds were assessed for total lipid content; production of the valuable omega-3 and omega-6 fatty acids, eicosapentaenoic acid and arachidonic acid; plant hormones relevant to agricultural fertilisers; as well as general protein and carbohydrate content, pigmentation (antioxidants) and ash/mineral content.

3.1. Lipid and High-Value Omega-3 Oil Content

The FAME analysis was used to assess the total lipid content of each seaweed species (Table 2). The total concentration of lipids in the seaweeds are small in comparison to most land-based plant species [16] and varies with seasonality, generally peaking in late summer, decreasing over the autumn and winter and increasing again in spring [17]. Our data reflects this, with lipid content ranging from 0.8% of dry biomass in *Colpomenia peregrina* to 2.9% in *Fucus serratus*. Whilst the overall lipid content was low, the proportion of commercially important long-chain polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and arachidonic acid (ARA) was high, suggesting some seaweeds may prove viable sources of high-value nutraceuticals, in a global market worth in the region of \$400 billion annually [18]. All of the seaweeds tested with the exception of *Ulva lactuca* showed high concentrations of ARA (C20:4) and/or EPA (C20:5).

Table 2. Fatty acid (FA) profiles of South West seaweed samples. Data, expressed as % of total FA content and total lipid, are given as mg/g and % of dry biomass.

	Fatty Acid (% Total FAME)										Total Lipid	
	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3 (γ)	C18:3 (α)	C20:4	C20:5	(mg/g)	(% Dry Biomass)
<i>U. lactuca</i>	0.0	36.4	0.0	9.1	18.2	18.2	0.0	18.2	0.0	0.0	18.09	1.8
<i>S. aeruginosa</i>	0.0	33.3	0.0	11.1	11.1	11.1	0.0	22.2	0.0	11.1	13.89	1.4
<i>P. rotunda</i>	10.0	30.0	0.0	10.0	10.0	0.0	0.0	0.0	20.0	20.0	12.92	1.3
<i>L. articulata</i>	14.3	28.6	0.0	14.3	14.3	0.0	0.0	0.0	14.3	14.3	12.15	1.2
<i>A. devoniensis</i>	11.1	22.2	0.0	11.1	11.1	0.0	0.0	0.0	22.2	22.2	12.36	1.2
<i>P. palmata</i>	7.1	21.4	0.0	7.1	7.1	0.0	0.0	0.0	7.1	50.0	23.25	2.3
<i>R. confervoides</i>	14.2	28.6	0.0	14.2	14.2	0.0	0.0	0.0	14.2	14.2	8.58	0.9
<i>D. carnosa</i>	9.1	27.3	0.0	9.1	9.1	0.0	0.0	0.0	18.2	27.3	18.83	1.9
<i>S. muticum</i>	8.3	25.0	8.3	8.3	8.3	8.3	0.0	8.3	16.7	8.3	15.79	1.6
<i>H. elongata</i>	7.7	23.1	0.0	7.7	15.4	7.7	0.0	7.7	15.4	15.4	19.26	1.9
<i>F. serratus</i>	12.5	20.8	4.2	4.2	25.0	8.3	0.0	4.2	12.5	8.3	29.13	2.9
<i>L. digitata</i>	8.3	16.6	0.0	8.3	16.6	8.3	0.0	8.3	16.6	16.6	15.62	1.6
<i>S. latissima</i>	8.3	16.7	0.0	8.3	16.7	8.3	8.3	8.3	16.7	8.3	18.52	1.9
<i>C. peregrina</i>	16.7	16.7	0.0	16.7	16.7	0.0	0.0	0.0	16.7	16.7	7.50	0.8
<i>P. latifolia</i>	8.3	16.7	8.3	8.3	8.3	8.3	0.0	8.3	16.7	16.7	16.48	1.6

Fish-derived oils (themselves a bioaccumulation of algae synthesised PUFAs) are currently the major source of omega-3 and omega-6 PUFAs [16,19]. Seaweed could provide a viable alternative source where, for example, in *Palmaria palmata*, despite having a lipid content of just 2.3% at the time of sampling, 50% (11.6 mg/g biomass) of this lipid was in the form of EPA (20:5). Given that the EPA content of commercially available fish oil supplements range between ~40–500 mg/g [20], it is clear that seaweeds could make a big impact as a substitute feed stock for the production of high-value omega-3 animal feed supplements, nutraceuticals, pharmaceuticals and cosmetics. Indeed, the recommended dietary ratio of ω-6: ω-3 PUFA is less than 10 [16] and with all of the seaweeds analysed here having a ratio of between 0.15 and 2, so offering a significant advantage to the food and feed industries.

Ulva lactuca (a common bloom forming species in the South West and globally) was the only seaweed tested which did not contain any EPA or ARA, although it did, however, contain a relatively high abundance of the essential fatty acid linoleic acid (18:2). The majority of the fatty acid content was palmitic acid (C16:0), which is used at high concentrations in products such as soaps and industrial

release agents. Given the lower economic value of these products and the low overall lipid content of *Ulva lactuca*, it is unlikely that this seaweed would be an economical alternative source, unless integrated into a biorefinery model with at least one higher value co-product.

3.2. Pigments

In 2016, the global pigment and dyes market was estimated to be valued at \$30.42 billion [21], and is expected to see significant growth in demand in the coming years. Whilst global omega-3 and omega-6 PUFA supplies are intrinsically linked with marine algae production, the pigment and dyes market is not as reliant on marine sources, and establishing seaweed-derived materials is more challenging. Nevertheless, seaweed pigments have found uses due to the fact of their antimicrobial properties [22], as well as uses in dyes, additives, health supplements, antibiotics, bioelectronics and antioxidants. The pigment content of each seaweed species was identified using HPLC. The primary pigments are given in Table 3. Levels of pigmentation varied both within taxon and among species. The lowest overall pigment content was seen in *Ahnfeltiopsis devoniensis* with just 37 µg pigment/g dry biomass whilst *Punctaria latifolia* had the highest content at 1319 µg/g.

Fucoxanthin, the xanthophyll responsible for the brown colouring of Phaeophyta, has been shown to have promising therapeutic uses in cancer and obesity treatments [23,24], as well as antibacterial properties [22] and could be beneficial in fertilisers, as it can help to reduce crop diseases. Unsurprisingly, whilst low levels of this pigment were observed in all the seaweeds analysed, only the browns contained it at concentrations that could be useful for industrial extraction, ranging from 340.4 µg/g in *Punctaria latifolia* to just over half this in *Fucus serratus* at 131.8 µg/g.

Product colour can have a huge impact on consumer perception, but concerns over the safety of synthetic colour additives and the increase in industrial safety requirements is leading the food and drink industries to increasingly seek natural colour alternatives [25]. Seaweed pigments range in colour from blue-greens (chlorophylls) to yellows (xanthophylls) and orange-reds (carotenes), and have a similar level of stability relative to their synthetic counterparts making them ideal as food colourings [26]. Chlorophyll (chl) is already approved and registered as a food additive (E140) and is used to colour various foods and beverages green [27] and has also been shown to have potential uses within cosmetics as deodorants and dentifrices due to the fact of its odour reducing properties [28].

As expected, both the levels and types of chlorophyll varied across the seaweed species tested. Both the green seaweeds had chl-b and chl-a at an approximate ratio of 1:1.5 (*Spongomorpha aeruginosa*) and 1:1.4 (*Ulva lactuca*). The red seaweeds generally contained predominantly chl-a, with very low levels (less than 10% of the chlorophyll pigment pool) of chl-c and/or chl-b. The exception was *Palmaria palmata* which contained chl-a only. The brown seaweeds all generally contained chl-c at levels of 12–22% than that of chl-a. The exceptions to this were *Fucus serratus* which had an approximately 50:50 ratio of chl-c:chl-a, and *Gastroclonium ovatum* whose chl-c accounted for just 0.5% of its total chlorophyll pigmentation.

The carotenoids α and β carotene are converted to vitamin A in the human body [29] and along with the xanthophylls lutein, zeaxanthin and violaxanthin, play a crucial role in maintaining eye health as well as reacting with free radicals to reduce oxidative stress and lipid peroxidation [24,30]. *Punctaria latifolia* contained the highest level of carotenoids at 46.8 µg/g, *Palmaria palmata* had the highest levels of lutein at 56.4 µg/g and *Gastroclonium ovatum* the highest levels of zeaxanthin at 11.8 µg/g. Violaxanthin was abundant in all the brown seaweeds with *Punctaria latifolia* containing 106.3 µg/g of this orange pigment.

Table 3. Primary pigments of South West seaweed samples ($\mu\text{g/g}$ dry biomass). Chlorophyll (chl)-c is given as the total of C-1, 2 and 3 subtypes.

	Pigment $\mu\text{g/g}$											Total Pigment
	Chl-c	Chl-b	Chl-a	Fucoxanthin	α Carotene	β Carotene	Lutein	Zeaxanthin	Neoxanthin	Violaxanthin	Antheraxanthin	
<i>U. lactuca</i>	0.0	110.6	155.0	2.3	0.8	8.4	34.0	1.5	80.2	17.3	0.0	422
<i>S. aeruginosa</i>	0.7	98.7	154.9	2.9	0.0	10.6	27.7	3.9	7.4	11.1	0.0	334
<i>P. rotunda</i>	0.7	2.8	76.6	3.6	4.1	2.8	15.2	0.8	0.0	0.4	0.0	129
<i>L. articulata</i>	0.0	2.6	119.7	4.1	7.7	1.0	19.4	0.8	0.0	0.0	0.0	173
<i>A. devoniensis</i>	0.0	1.6	26.3	0.9	0.6	1.4	5.0	0.8	0.0	0.0	0.0	37
<i>P. palmata</i>	0.0	0.0	213.1	6.2	12.1	11.0	56.4	1.1	0.0	1.5	0.0	315
<i>R. confervoides</i>	5.7	4.0	179.0	22.6	5.7	7.9	29.4	2.0	0.0	1.4	2.5	270
<i>D. carnososa</i>	0.0	10.1	133.6	1.9	11.6	5.9	33.9	0.0	1.2	0.7	0.0	271
<i>Calliblepharis</i> spp.	0.9	5.9	197.5	4.6	9.1	9.6	44.1	0.8	0.0	0.0	0.0	283
<i>S. muticum</i>	99.2	2.1	473.5	292.7	0.0	35.7	0.7	10.2	0.0	80.2	38.6	1045
<i>H. elongata</i>	52.8	0.0	379.5	195.7	0.0	27.0	0.3	3.1	0.0	64.9	21.0	749
<i>F. serratus</i>	32.1	0.0	62.5	131.8	0.0	13.4	0.4	1.5	0.0	53.7	14.9	313
<i>L. digitata</i>	65.4	0.0	387.1	230.8	0.0	20.6	0.3	2.7	0.0	57.4	28.9	801
<i>S. latissima</i>	73.0	0.0	462.6	298.2	0.0	17.7	0.5	7.7	0.0	36.9	34.3	945
<i>P. latifolia</i>	139.0	0.0	612.7	340.4	0.0	46.8	0.5	6.8	0.0	106.3	54.1	1319
<i>C. peregrina</i>	8.5	1.0	70.7	38.8	0.0	1.9	0.9	1.0	0.0	6.6	4.7	135
<i>G. ovatum</i>	1.8	0.0	337.0	7.6	6.4	27.1	71.3	11.8	0.0	0.0	1.3	484

Antheraxanthin, a keto-carotenoid and yellow colorant, has a range of benefits to human and animal health. Due to the fact of its high demand in the pharmaceutical, nutraceutical, food and feed industries, there are major efforts to improve antheraxanthin production from biological sources instead of synthetic ones [31]. None of the green and only one of the red seaweeds (*Rhodomela confervoides*) contained antheraxanthin and this was at a very low level of just 2.5 µg/g. All of the brown seaweeds analysed contained antheraxanthin, but the content varied from 1.3 µg/g in *Gastroclonium ovatum* to 54.1 µg/g in *Punctaria latifolia*.

Overall, from a commercial perspective, *Punctaria latifolia* has good levels of all the important pigments (with the exception of lutein) making it an ideal candidate for multi-pigment isolation. Lutein production would be best achieved with *Palmaria palmata* which would also generate chlorophyll-a as a secondary pigment product.

3.3. Macronutrients—Carbohydrate and Protein

Many types of useful carbohydrates such as laminarin, cellulose, starch, alginate, fucoidan, agar and carrageenan are found in seaweed. Agar, alginate and carrageenan are all used within the food industry as thickening agents within food [10] and are currently the most commercially significant products from seaweed after direct consumption as food [5]. Crucially, they are all produced in single product-based industrial processes, rather than in the biorefinery approach explored herein. Beyond the food ingredients industry, seaweed biomass with high carbohydrate content can be used for production of biofuels by anaerobic digestion and fermentation converting the sugars to ethanol or butanol. Seaweeds were initially assessed for the total carbohydrate content using a traditional phenol-sulphuric acid method in which polysaccharides are broken down to monosaccharides, dehydrated to furfurals and reacted with phenol to produce a measurable colour.

Although the method detects almost all carbohydrates, the sensitivity varies depending on the type of sugars present [6] since the absorptivity of the different carbohydrates varies somewhat.

Thus, unless a sample is known to contain only one carbohydrate, the results must be expressed arbitrarily in terms of one carbohydrate (in this instance we used glucose). We found this method to be very unreliable due to the variations in carbohydrate structures found in seaweeds and, as such, we instead estimated the total carbohydrate content based on the protein, lipid and ash values (Table 4).

Table 4. Carbon (C), nitrogen (N), protein, carbohydrate and ash content of seaweeds from South West England.

	Component % of Dry Biomass				
	C	N	Protein	Ash	Carbohydrate
<i>U. lactuca</i>	30.8	1.09	5.45	22.7	71.8
<i>S. aeruginosa</i>	20.3	1.06	8.01	46.4	45.6
<i>P. rotunda</i>	31.0	3.53	17.65	29.6	52.7
<i>L. articulata</i>	20.2	2.75	13.77	50.1	36.2
<i>A. devoniensis</i>	31.8	1.87	9.37	24.2	66.4
<i>P. palmata</i>	38.3	2.5	12.50	21.4	66.1
<i>R. confervoides</i>	26.2	2.51	12.54	45.8	41.6
<i>D. carnosa</i>	36.3	2.91	14.55	18.2	67.2
<i>S. muticum</i>	34.5	1.39	4.64	26.4	69.0
<i>H. elongata</i>	35.8	1.13	5.65	24.6	69.7
<i>F. serratus</i>	39.3	1.8	8.98	21.5	69.5
<i>L. digitata</i>	34.2	1.37	6.87	27.8	65.3
<i>S. latissima</i>	36.2	1.21	6.03	20.9	73.0
<i>C. peregrina</i>	13.8	0.58	2.48	85.3	12.2
<i>P. latifolia</i>	28.8	1.15	5.73	43.8	50.5

Nine of the seaweeds tested had an estimated carbohydrate content of over 60%, with the highest observed in *Saccharina latissima* (73.0%).

Colpomenia peregrina had the highest ash content and was particularly mineral rich resulting in a much lower carbohydrate content (estimated at 12.2%).

The CHN analysis was used to calculate the protein content of the seaweeds. As well as protein being an important part of a healthy diet, nitrogen is an important component needed for plant growth; seaweeds with a high nitrogen content work well as sustainable sources of nitrogen for fertilisers [32]. With the exception of *Fucus serratus*, the highest concentrations of nitrogen/protein were observed in the Rhodophyta ranging from 9.37–17.65% of the total dry biomass. All of the seaweeds, however, have a nitrogen content that can make them suitable as a feed stock for the sustainable production of agricultural fertilisers.

3.4. Minerals

The ash content of the seaweeds ranged between an 18.2 and 85.3% dry biomass weight (Table 4). High ash content is indicative of high levels of minerals and trace elements [32] which are beneficial in fertilisers as a sustainable source of essential nutrients required for plant/crop growth/development. However, high levels of metal can be an issue when used as a food source or as fertilisers if they are found at unacceptably high levels. Indeed, some species of seaweed can perform a bioremediation service within metal-polluted waters, and seaweed harvested from such environments may be unsuitable for use in food or fertilizer without costly processing to remove heavy metals [33]. However, conversely, the bioremediation opportunities for seaweeds within aquatic systems may offer a significant and valuable upstream “service product” within a biorefinery process, subsidising the production of lower value downstream products.

X-ray fluorescence spectroscopy was used to assess whole dry biomass for the presence of a range of minerals (Table 5). Demand for phosphorus is expected to outstrip supply as soon as 2035 [34]. An estimated 80–90% of phosphorus use is in the form of fertiliser production with much of this then being lost through leaching from the soils [35]. Seaweeds can make an excellent alternative to current commercial fertilisers because of trace nutrients such as phosphorus and nitrogen, as well as the presence of hormones that can encourage plant growth. Seaweeds can, however, also rapidly accumulate pollutants, such as dissolved metals from their environment [36], or become loosely or transiently associated with metal particulates. As such, composition analysis of this nature must be taken with a pinch of (metallic) salt, as even the smallest metallic fragment derived from, for example, litter, fishing or structural material could give a potentially misleading result.

Table 5. Mineral composition of seaweeds from South West England (ppm). One ppm is equivalent to 0.0001% of total dry biomass.

	Mineral (ppm)										
	Fe	Sn	Mn	Al	Si	K	P	S	Ca	Cu	Zn
<i>S. aeruginosa</i>	620	0	0	1120	2530	35,020	910	1070	7370	0	10
<i>L. articulata</i>	4040	0	260	9090	74,010	16,320	3010	1290	46,780	0	80
<i>A. devoniensis</i>	180	20	70	230	1980	30,480	1430	390	12,720	0	20
<i>P. palmata</i>	0	0	30	0	0	105,740	2390	0	2550	0	10
<i>R. confervoides</i>	900	0	1420	1740	6450	77,280	1970	260	11,960	0	200
<i>D. carnosa</i>	0	70	0	0	0	41,130	1650	0	9030	0	10
<i>C. spp.</i>	1320	0	160	2290	12,400	25,130	1620	1400	16,250	0	20
<i>S. muticum</i>	80	60	10	280	1990	75,760	1340	0	11,200	0	10
<i>H. elongata</i>	0	0	20	200	1350	72,290	1140	0	7530	10	20
<i>F. serratus</i>	440	0	10	730	3950	34,320	890	730	5110	0	10
<i>L. digitata</i>	210	30	10	120	2800	34,560	2850	0	3160	0	20
<i>S. latissima</i>	120	10	70	0	0	39,460	1670	0	8670	0	30
<i>P. latifolia</i>	260	20	10	510	7420	123,530	1270	420	12,340	0	30
<i>C. peregrina</i>	9310	50	230	19,610	252,290	46,930	670	3350	55,640	20	50

The phosphorus content in the seaweeds analysed ranged from 0.1 to 0.3% of dry biomass—ideal for fertilizer products. However, the presence of aluminium was observed in all but three seaweeds, and whilst this is not unusual [37], if used as a fertiliser, over time soils could become contaminated with elevated levels of aluminium which in acidified soils can lead to plant toxicity [38]. Transition metal molybdenum and heavy metals arsenic and lead were not observed in any of the samples which is testament to the water quality on the South West coast where the sampling took place.

Colpomenia peregrina had a consistently high mineral content across the board and was one of just two of the seaweeds assessed to contain copper at detectable levels. This was not unexpected since this seaweed grows best when attached by rhizoidal filaments to rock bed or molluscs such as oysters from which minerals are leached.

Manganese was detected in most of the seaweeds and was particularly high in *Rhodomela confervoides* at 0.142% of the dry biomass. Whilst this mineral is important in many industrial processes, such as metal alloy manufacture, it is also widely used in nutritional supplements.

All of the seaweeds analysed contained detectable zinc and all but three of the seaweeds had iron at levels that could be used easily in nutritional supplements (the total daily recommended intake of iron is just 8.7–14.8 mg/day). It should be noted that the highest levels of this metal were observed in the physically smaller seaweed species such as *Lomentaria articulata* (4 mg/g) and *Colpomenia peregrina* (9.3 mg/g).

3.5. Phytohormones

In the agricultural industry, phytohormones have several commercial uses that are related to plant growth, flowering, ripening and alleviation of abiotic stresses such as drought, heat, cold, light and nutrient stress. Synthetic phytohormones have been used in agriculture for over 50 years with great success, but recent changes in regulation and consumer preferences have created a greater need for natural and sustainable alternatives. Whilst high-purity extracts may or may not prove a viable high-value product in a seaweed biorefinery in their own right, their presence in fractions to be used as agricultural fertilisers, soil conditioners and bio-stimulants could provide an economic premium for such products. Cytokinins (including TZR, CZR and 2iP) are amongst the most valued phytohormones in agriculture as they are directly related to plant growth, flowering and fruit set, and there are currently not many natural sources available in the market.

The levels of four different bioactive molecules (i.e., abscisic acid (ABA), trans-zeatine riboside (TZR), cis-zeatine riboside (CZR) and N6-(2-isopentyl) adenosine (2iP)) within the dried seaweed biomass was assessed (Figure 1). The levels of phytohormones were species specific and there was no trend with taxa, and whilst several seaweeds showed strong phytohormone production, four had levels that were extremely low and not of any commercial relevance. The highest level of ABA was seen in *Ulva lactuca*, which also had strong levels of TZR, CZR and 2iP. *Sargassum muticum* and *Himanthalia elongata* both had high levels of 2iP and TZR, whilst CZR was highest in *Ulva lactuca* and *Rhodomela confervoides*.

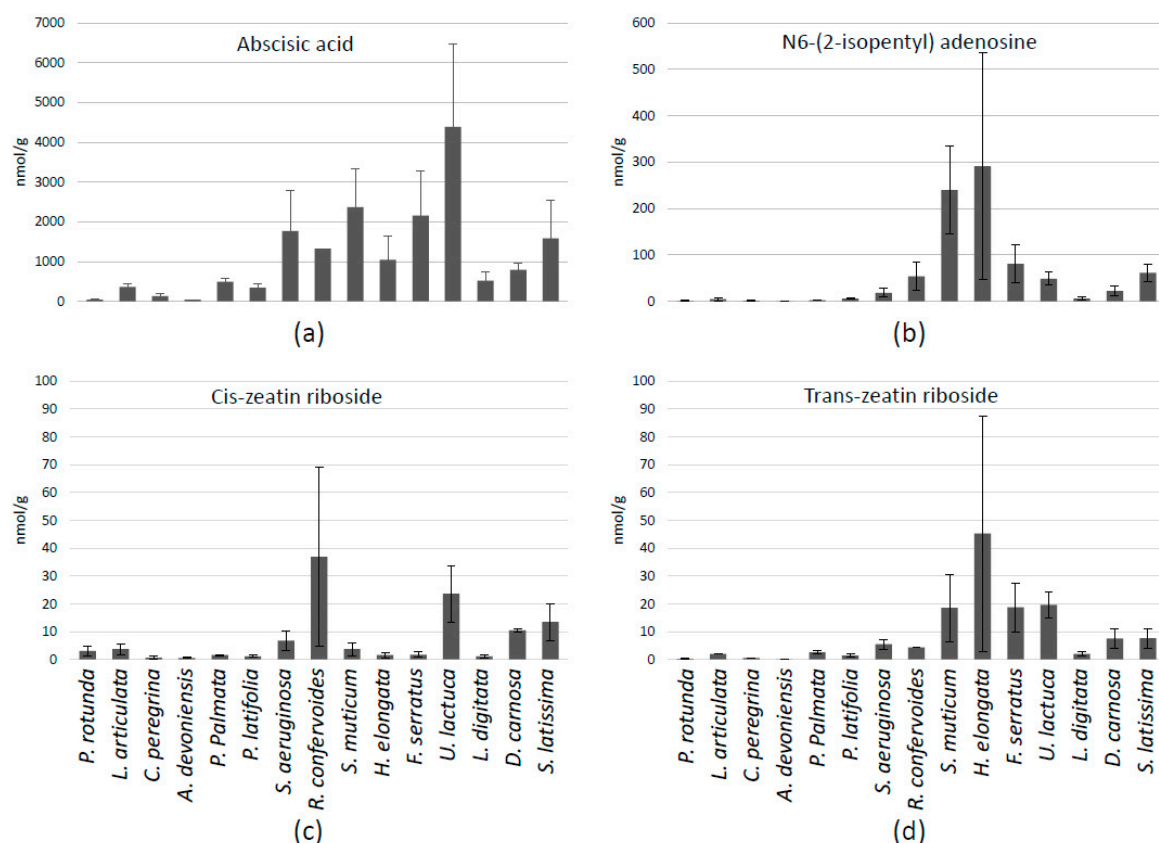


Figure 1. Levels of four phytohormone levels in South West seaweeds (SD error bars shown). (a) absciscic acid (ABA); (b) N6-(2-isopentyl) adenosine (2iP) (c) cis-zeatin riboside; (d) trans-zeatin riboside (TZR).

4. Conclusions

Seaweeds contain many varied and commercially valuable elements from individual pigments through to the whole biomass, and yet they remain an under cultivated and underutilised commodity. Currently, commercial exploitation of seaweeds is mostly limited to whole biomass consumption or single product extracts for the food industry. The development of a seaweed biorefinery, based around multiple products and services, could provide an important opportunity to exploit new and currently underexplored markets. This is especially so within countries such as the UK which have large stretches of coastline where natural harvest or commercial cultivation could be carried out alongside other marine activities such as windfarms. By taking a holistic biorefinery approach to fractionate and utilise multiple components of the biomass, not only can a significant level of revenue be achieved, but seaweeds may fuel the replacement of synthetically manufactured compounds often derived from petroleum oils. We have demonstrated in this work that native and invasive seaweeds on the South West coast contain valuable products and have the potential to be exploited through a biorefinery pipeline.

Seaweed is a primary food source in many Asian countries, but with very little consumed in western diets. Seaweeds can be, without doubt, nutritious due to the high abundance of pigments and oils that are beneficial to our health. This can be exploited by both the artisanal food and traditional food industries in Europe and beyond. However, the shift in cultural attitude required for greater consumption of seaweed-derived foods may hinder the expansion of this market in the west. A biorefinery approach, generating multiple high to low value products for multiple markets (such as pigments, PUFAs, high-quality fertilisers), could alleviate limitations to expansion of these traditional industrial seaweed activities. Indeed, a more radical approach than that outlined here employs hydrothermal processing of biomass or extracts to create multiple low-value product streams.

As an established industrial process, such processing can be applied to “waste” fractions generated after high-value products have been isolated in a seaweed biorefinery, providing an intrinsic value to every component of the biomass. Hydrothermal liquefaction (HTL) uses a high-temperature and -pressure process to convert any biomass in to four primary outputs—bio crude oil, gas, ash (from which metals can be recovered) and an aqueous fraction (to which soluble minerals such as nitrogen, phosphorus and potassium partition) and is an excellent example of a biorefinery process. Indeed, two of the seaweeds (*Ulva lactuca* and *Sargassum muticum*) harvested as part of this study were subject to HTL in a separate investigation [39], suggesting that extracts derived from their whole biomass of insufficient value or of no obvious market can be successfully converted into low-value products with established markets. Here, we have shown that the seaweeds of the South West coast, seaweeds which are currently overlooked, unexploited and often unappreciated, naturally contain a plethora of metabolites and compounds with high commercial relevance and interest. Individually, they are unlikely to reach commercial exploitation, yet when exploited together in a biorefinery approach, the potential exists for a burgeoning seaweed-based bio-economy to develop in areas such as the South West of the United Kingdom.

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